Detailed Description of the Invention]
[0001]
[Field of the Invention]In this invention, material to be coated is immersed in the colloidal solution of the metal particles which embellished the metal particle surface with the organic compound, and it irradiates with the laser beam which excites metal particles.
Therefore, it is related with the method of fixing metal particles to this coating material-list side.

[0002]
[Description of the Prior Art]As material, for example, the conventional method which forms golden particles in the surface of a substrate, to be coated, 1. How to carry out the cast of colloidal solution which made organic solvent distribute golden particles, and to dry it, 2. How to make golden particles adsorb by electrostatic interaction on poly cation made to stick to glass surface etc., or cationic molecular film, Although 3. substrate face is embellished with a thiol derivative (processing) and there are a method of making golden particles fix using spontaneous bonding between golden-sulfur, etc., It is difficult for there to be a problem to the health by the volatilizing solvent in 1., and to make still more arbitrary shape fixed, and it is the necessity of processing the substrate face by the ornamentation agent beforehand in 2. and 3. 4. Although the method of accumulating golden particles on an electrode with an electrophoresis method is also developed these days using golden particles being charged in negative, a substrate is limited to conductivity.
[0003]It is known that precious-metals particles (tens of nm - several nanometers), for example, golden particles, such as Au, Ag, and Pt, will absorb the laser beam of an ultraviolet area - a near-infrared region, and both the phenomena of division (distribution) of condensation of particles and particles will appear as a result.
[0004]By the way, the surface treatment by metal is used also for manufacture of various functional members. For example, the Teflon porous electrode is obtained by processing Teflon porous membrane with a metallic material, and. The surface enhancement Raman (Surface Enhanced Raman Spectroscopy: SERS) sensor board is obtained by carrying out vacuum deposition of the metal to island shape thinly in a substrate face. Therefore, it is recognized that development of the new surface treatment art by metal is important also in respect of development of a member with a new function.
[0005]
[Problem(s) to be Solved by the Invention]The technical problem of this invention is providing the adherence method of metal particles without the inconvenience in the adherence method of said conventional metal particle of using the problem to health, and special processing as a substrate face beforehand, and there is in providing the adherence method of metal particles that a member with still newer functionality is obtained. The place wholeheartedly examined based on the idea whether a phenomenon when it irradiates with laser is inapplicable to the colloidal solution of said metal particle although said technical problem is solved, Where the material by metal which should be carried out surface treatment is immersed in the colloidal solution of metal particles, By irradiating with the laser beam of an ultraviolet area - a near-infrared region the surface of said colloidal solution and said material which should be processed, it discovers that metal particles are fixable to the surface of said material which should be processed, and said technical problem is solved. Said phenomenon could be applied without being limited to the material which constitutes a substrate, and it was discovered as a transparent substrate that not only glass but it can apply to a substrate [non-conductive /, such as a

fluorine system high polymer film, / and inertness].
[0006]
[Means for Solving the Problem]This invention dips material to be coated into a colloidal solution of metal particles, It is the method of fixing metal particles to this coating material-list side by irradiating the surface of said solution and material to be coated with a laser beam which excites said metal particle, A colloidal solution of metal particles combines with the less than 100-nm metal particle surface of 1 nm or more preferably a colloid stabilizing agent which is an organic compound, It is how to fix to a coating material-list side said metal particle distributing in an organic solvent, a laser beam is in an ultraviolet area - a near-infrared region still more preferably, and it is pulse width. It is 5 ns - 10 ns, and pulse energies are 20mJ - 400mJ. [20mJ - 400mJ / pulse (pulse)] -- it is -- it is the method of fixing to a coating material-list side said metal particle characterized by things. This invention solved said technical problem by discovering that there are a deposit and an adherence phenomenon of metal particles to said base surface by laser beam exposure from a colloidal solution which combined with the metal particle surface a colloid stabilizing agent which is an organic compound. It does in this way, and size of metal particles which adhered is an average of about 10 nm (being 30 nm or less in general), and it is expected that functionality as a resonance Raman sensor is improved.
[0007]
[A mode of operation of this invention] This invention is explained more to details.
A. Stabilize the metal particle surface (50 nm - 5 nm) preferably with a colloidal solution of metal particles used by this invention with a stabilizing agent with a particle diameter of 1 nm - 100 nm separated from said metal particle surface by laser beam exposure. A thing which constitutes such a material and which plasmon excitation, such as Ag, Au, and Cu, tends to start as metal can be mentioned as a desirable material. Thiol compounds which are sulfur atom content organic compounds solubilized to an organic solvent as a stabilizing agent, such as dodecanethiol, fatty acid, such as oleic acid, etc. can be mentioned.
B. As a solvent to distribute, hydrocarbon, such as aromatic series, such as alicyclic of aliphatic series, such as hexane, cyclohexane, etc., benzene, and toluene, can be mentioned.
[0008]C. Metal particle fixed phenomenon to a substrate face of a laser beam and metal particle colloid. Being able to use a laser beam of an ultraviolet area - a near-infrared region for immobilization in a substrate face of said metal particle, especially use of a pulse laser beam is an efficient method. As a pulse laser beam, a fundamental wave of Nd:YAG laser (1064 nm), A thing of a double wave (532 nm), three double waves (355 nm), 5 ns - 10 ns of width and pulse energy 20mJ - 400mJ is useful to immobilization of metal particles from metal particle colloid by a laser beam to a substrate face.
[0009]D. Explain theoretically a deposit and a fixing method of metal particles from metal particle colloid of this invention to a substrate face to drawing 1. A pulse laser from a pulse laser generating means (L. R) is irradiated via a mask (M. S) by a substrate to be coated and metallic colloidal solution by which a glass substrate (B. P) is specifically immersed. Metal particles (M. P.L) are fixed to said irradiated substrate face. A process of immobilization of said metal particle can be carried out also by operating a laser beam according to a desired drawing figure via a mask. Drawing 2 is a scanning electron micrograph (SEM image) of golden particles (M. P.L) fixed corresponding to a mask. A round white thing is the gold colloid deposited and fixed. It is guessed that a difference in particle diameter is a thing also depending on particle size distribution of golden particles before a laser beam exposure. ****** by which drawing 3 is an absorption spectrum of gold colloid adhering to a glass surface by

laser radiation, and a plasmon band of golden particles is observed near 540 nm. E. As a pulse laser generating means, Nd:YAG laser (wavelength of 1064 nm, 532 nm, 355 nm), other titanium:sapphire laser, an excimer laser, etc. can be used.

[0010]A phenomenon of a deposit and immobilization of metal particles from said metallic colloid is a phenomenon accompanying photon absorption of metallic colloid. It is known that golden particles which absorbed a photon by the exposure of a pulse laser beam will cause a rapid rise in heat. Some stabilizing agents (protecting agent) which have adhered to the particle surface as a stabilizing agent in that case separate with light, and it is considered that dispersion stability is lost. As a result, destabilized particles which exist near the base are considered to stabilize by fixing in a base. On the other hand, in a solution, it is thought that condensation and growth of particles by said phenomenon also advance. Therefore, immobilization is considered to be influenced by a stabilizing agent and solvent to be used.

[0011]

[Example]Example 1 Production of fixed A. gold colloid of golden particles.

The gold colloid solution was obtained by the method (J. Phys.Chem., 99, 7036 (1995)) of reflex (Leff) and others of returning chloroauric acid with sodium borohydride. As a result of measuring with a transmission electron microscope (TEM), the mean particle diameter of golden particles was 3-4 nm. B. Optical fixing method Said produced gold colloid was dissolved in cyclo hexane, and it was considered as the colloidal solution (M. C.S). Put this solution 3mL into the quartz cell (4x1x4 cm) for fluorometry (SE), dip a glass substrate (B. P) (2x2x0.02 cm) into a solution, and under 20 ** temperature, It irradiated with the pulse laser beam (Nd : the number of repetitions of an YAG laser, the wavelength of 1064 nm, pulse width 5-7ns, pulse energy 260mJ, 10 Hz). The immobilization to a glass surface can be checked now in about 10 minutes. desorption came to be accepted, when about 1 law was reached and it glared more in 20 to 30 minutes. The glass substrate was taken out and adhesion (M. P.L) of golden particles was checked by only the laser beam irradiation part. Adhesion of golden particles was checked by only the laser beam irradiation part also about the quartz cell. Measurement of the absorption spectrum of the glass substrate observed the plasmon band characteristic of golden particles near 540 nm (drawing 2). Said golden particle was uniformly arranged on the glass substrate, and the surface made rude was observed. although the glass substrate was immersed into toluene and nitric acid, saw desorption of golden particles and it was not stopped. Desorption was not clearly accepted by ultrasonic irradiation. That is, it was checked that golden particles are being fixed on a glass substrate by the adhesion force from which it is not desorbed by mechanical power.

[0012]Operation of Example 1 was repeated only by replacing example 2 substrate with a calcium fluoride board. The same result was obtained also with the calcium fluoride board (1.8 cm in diameter, and 0.1 cm in thickness).

[0013]Operation of Example 1 was repeated only by replacing example 3 substrate with a Teflon membrane filter. The gold grain was fixed to the shape of the laser beam which irradiated also with the Teflon membrane filter (Millipore Corp. DEYURAPOA VVLP, 100 nm in aperture). It became clear that the particles fixed from absorption-spectrum measurement are particles (mean particle diameter of about 10 nm) of the gold distributed in colloid.

[0014]The wavelength of the laser beam with which it irradiates example 4 was changed, and operation of Example 1 was repeated. The double wave of Nd-YAG laser It became clear using the laser beam of [532 nm, 38mJ / pulse (pulse)] that golden particles are fixable on a glass substrate.

[0015]The wavelength of the laser beam with which it irradiates example 5 was changed, and operation

of Example 1 was repeated. Three double waves of Nd-YAG laser It became clear using the laser beam of [355 nm, 20mJ / pulse (pulse)] that golden particles are fixable on a glass substrate.

[0016]It is known for the substrate which made the metaled surface rude that the Raman scattering intensity of the substance to which it stuck will increase dramatically. This phenomenon is called surface enhancement Raman (Surface Enhanced RamanSpectroscopy:SERS). As such the surface, the gold which etched the surface, the silver substrate, and the substrate which carried out true steaming-of-printing-steamer work very thinly so that metal might adhere to island shape have been used until now. However, it is clarified that the substrate which arranged metal particles in two dimensions by one side is the most effective as a SERS sensor board. In order to arrange golden particles in a substrate face conventionally, the mutual adsorption process and the LB method can have and can be, but by any technique, a lot of organic matters exist near the gold grain, and need to process a substrate face by an ornamentation agent beforehand. In the metal fixed board created by this technique, particles are only further surrounded by the organic compound, and the organic molecule can still be stripped off from a gold surface by nitric acid treatment. It is thought that the metal particle fixed board with the clean surface acquired can give the susceptibility which is not in the former as a SERS sensor board, and a selection system.

[0017]

[Effect of the Invention]As stated above, the fixing method of the metal particles of this invention, By using as that it can apply without being limited to a substrate material, and a laser means combining the thing for immobilization of the metal particles by this invention, and the thing of a thermal melting arrival operation etc., The effect excellent in the point which can consider application to things, such as manufacture of said SERS sensor board and manufacture of a porous electrode, is brought about.